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## Nonlinear Optical Properties of Conducting Polymers

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Institute for Polymers and Organic Solids  
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This contract was for Fellowship support for S. D. Phillips during the period of his thesis research. Phillips has completed the dissertation research and he has submitted the dissertation to the University of California as partial fulfillment of the requirements for the PhD degree. Phillips is scheduled to defend his thesis on May 4, 1989.

Phillips dissertation bears the following title:

### **Photoconductivity and Electroabsorption in Conjugated Polymers**

Copies of the title page and the dissertation abstract are included as a part of this report.

During the period of this fellowship support, Phillips completed and published a number of articles in major scientific journals. These are listed as follows:

Transient Photoconductivity in Oriented trans-Polyacetylene Prepared by the Naarmann-Theophilou Method, Phys. Rev. B38, 6211 (1988)

Metal-Polymer Schottky Barriers on Cast Films of Soluble Poly(3-hexylthiophenes), Synthetic Metals, 21, 379 (1987)

Metal-Polymer Schottky Barriers on Processible Polymers, Synth. Met. 28, C687 (1989)

Transient Photoconductivity in Conjugated Polymers, Synth. Met. 28, C669 (1989)

Electroabsorption and Nonlinear Optical Constants of Trans-Polyacetylene and Poly(3-hexylthiophene), Synth. Met. 28, D663 (1989)

Spectroscopy and Transient Photoconductivity of Crystalline Polyaniline, Phys. Rev. B (in press).

Localization of Charged Excitations in Polyaniline, Synth. Met. (in press).



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UNIVERSITY OF CALIFORNIA  
Santa Barbara

**Photoconductivity and Electroabsorption  
in Conjugated Polymers**

A Dissertation submitted in partial satisfaction  
of the requirements for the degree of

Doctor of Philosophy

in

Physics

by

Steven D. Phillips

Committee in charge:

Professor Alan J. Heeger, Chairman

Professor William C. Walker

Professor Philip A. Pincus

May, 1989

# Photoconductivity and Electroabsorption in Conjugated Polymers

by

Steven D. Phillips

## ABSTRACT

This dissertation presents the results of transient (subnanosecond) photoconductivity and electroabsorption spectroscopy of a variety of organic conjugated polymers. Although these two techniques may initially appear unrelated they actually probe many of the same quantities. In particular it will be shown that both techniques can provide information regarding the intrinsic anisotropy of quasi-one-dimensional polymeric systems. In addition, both experiments provide a sensitive measure of sample quality.

Transient photoconductivity measurements performed on oriented *trans*-polyacetylene prepared by the Naarmann-Theophilou synthesis, which results in samples containing a relatively low defect content, show a large long-lived, temperature-dependent photocurrent not seen in *trans*-polyacetylene prepared by other synthesis methods. By a comparison of the data to that obtained from high-quality single crystals of polydiacetylene, it is concluded that this long lived photocurrent implies a higher-quality polyacetylene. The anisotropic behavior for different polarizations of the incident light is presented together with the effect of light intensity, temperature and external field strength.

The results of spectroscopy and transient photoconductivity measurements on polyaniline in the fully reduced ("leucoemeraldine") and in the emeraldine base form are reported. A relatively strong photoconductive response is observed from pumping at 3.7 eV into the  $\pi - \pi^*$  absorption of leucoemeraldine, and a smaller photocurrent from pumping (at 1.9 eV and 3.7 eV) into the absorptions which characterize the emeraldine base. The results are interpreted in terms of the one-dimensional band structures calculated for the two forms of polyaniline.

Electroabsorption measurements are presented for unoriented *cis* and *trans*-polyacetylene and for oriented *trans*-polyacetylene. The electroabsorption spectrum of the unoriented material consists of a series of field induced absorptions and bleachings occurring at the band edge. In oriented *trans*-polyacetylene with the electric field parallel to the chain axis, the strongest of these features, which is often observed as a "knee" near 1.5 eV in the absorption spectrum, is highly suppressed, while the induced absorption at 1.28 eV is enhanced relative to the unoriented case. No electroabsorption signal is present when the external field is applied perpendicular to the chain direction. The dependence of the electroabsorption spectrum on temperature, electric field strength, incident light polarization and intensity is also described. An interpretation of the electroabsorption spectrum as electric field broadened, excited state phonon modes, is discussed.